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SUPERCONDUCTING MATERIALS : SOME RECENT DEVELOPMENTS

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SUMMARY

This review concentrates on four subject areas which have seen significant changes in recent years; AC losses, stability, multifilamentary Nb_3Sn and multifilamentary V_3Ga. Several applications are now being considered in which a small amplitude AC field is superposed on a larger DC field; fine filaments may not always give the lowest hysteresis loss under these conditions. The theory of self field instability has recently been improved and extended to the point where it can provide a good picture of the instability process under realistic thermal conditions. Some points of disagreement with experimental observation remain however, a possible explanation is offered for this. Multifilamentary Nb_3Sn and V_3Ga are now reaching the stage of meriting serious consideration as fully practical magnet conductors. The remaining problems of production and utilization are being solved and composites have been tested with at least twice the overall current density of filamentary NbTi at all field levels.

1. INTRODUCTION

The whole field of superconducting magnet materials has become so wide and diverse that a comprehensive review would now require very much more space than is available here. Such an all-embracing review has not therefore been attempted, but instead four subject areas have been chosen which have seen significant changes since the last Magnet Technology Conference. Each of these subjects has then been dealt with in some depth. For a more complete coverage of the field, the reader is referred to the recent review by Fietz and Rosner(1).

Two of the subject areas are theoretical: AC losses and stability. Although the theory of AC losses has not basically changed, several of the more recent applications have imposed different AC conditions and the conventional wisdom that 'finest filaments are best' may not always be true in this case. Stability theory has progressed in recent years and we now have a much better picture of the self field instability although there are still some areas of uncertainty and disagreement with experiment; a possible explanation for this is offered.

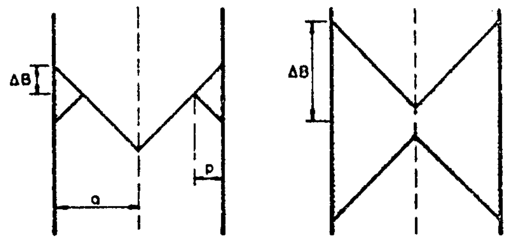
The two remaining subject areas are concerned with materials technology - more specifically with the production and utilization of multifilamentary composites of Nb_3Sn and V_3Ga. Good progress has been made in recent years and both materials are rapidly advancing to the stage where they must merit serious consideration by the magnet technologist as fully practical magnet conductors.

2. AC LOSSES

The multifilamentary composites which are now in general use were originally developed to eliminate flux jumping instabilities in the superconductor and thus promote stable operation in a magnet. The filaments were subsequently made finer and the coupling between them was reduced by the use of cupro-nickel barriers etc. so that the composites could be pulsed with a minimum hysteresis loss. The objective of this work was, and still is to a large extent, the development of a superconducting synchrotron. In a synchrotron, the magnets are pulsed from a low field to their maximum field and then to the low field again. Under these conditions, it is easy to show that the hysteresis loss in a superconducting magnet may be minimized by making the filaments as small as possible. In fact the loss per unit volume is simply proportional to the filament diameter, provided the filaments are sufficiently de-coupled from each other. Any coupling between the filaments will tend to increase the loss and so the coupling must be kept to a minimum by tightly twisting the composite and interposing resistive barriers between the filaments. A range of sophisticated composites has thus been developed to have minimum hysteresis loss in a synchrotron magnet or any other application (e.g. energy storage) where the field must be pulsed from zero to maximum or vice versa.

Recently however, another class of applications has emerged in which the superconductor is subject to alternating fields of a different kind. In this case, the major component of field is a steady DC level, but there is superposed on this an AC component of much smaller amplitude. Such conditions can occur for example in the DC rotor windings of a superconducting alternator or in the lift magnets of a magnetically levitated vehicle as it encounters irregularities in the guide way. They may also occur in some kinds of proposed fusion reactor where a single pulse of field may be applied, in addition to the DC containment field, to ignite the plasma. It has often been assumed that the low hysteresis composites developed for the synchrotron application will also be the best choice here, but it has recently been pointed out(2) that this is not necessarily so.

Adopting the simple one dimensional slab model of a superconducting filament, illustrated in Figure 1, we may distinguish two cases. Firstly, as shown in 1(a), the case where the disturbance caused by the fluctuating component of the field does not penetrate to the centre of the filament and there is in fact no loss in the centre. Secondly, as shown in 1(b), the disturbance penetrates the whole filament.



(a) below full penetration (b) above full penetration

FIG. 1. Slab model of AC field patterns (shaded area depicts flux change)

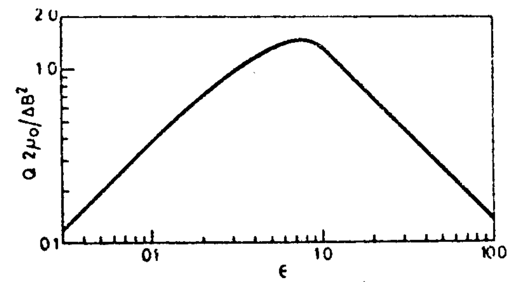


FIG. 2. Dimensionless loss per cycle $Q.2\mu_o/\Delta B^2$ versus dimensionless half width $\epsilon = a/p$.

In the first case, the loss per unit volume for a complete cycle may be shown to be

$$Q = \frac{2\Delta B^3}{3\mu_o^{\,2} J_c a}$$

where ΔB is the amplitude of the AC component of field, J_c is the critical current density and a is the half width of the slab. If the penetration depth of the AC field is p i.e. $\mu_o J_c p = \Delta B$, we may define a dimensionless half width $\epsilon = a/p$ and obtain the loss per cycle as Q

$$Q = \frac{\Delta B^2}{2\mu_o} \left\{ \frac{4}{3\epsilon} \right\}$$

Similarly, in the fully penetrated case we find

$$Q = 2\Delta B a J_c - \frac{4\mu_o J_c^{\,2} a^2}{3}$$

which may be written

$$Q = \frac{\Delta B^2}{2\mu_o} \left\{ 4\epsilon - \frac{8\epsilon^2}{3} \right\}$$

We may thus plot a 'dimensionless loss' $Q.2\mu_o/\Delta B^2$ as the simple function of ϵ shown in Figure 2.

It may be seen that, for a given field amplitude, the loss is a maximum when the superconductor half width is slightly less than the penetration depth of the superconductor. In the synchrotron case, where the penetration depth is large, ϵ is small and one is working at the left hand side of the peak. The most effective way of reducing losses will thus be to make ϵ as small as possible i.e. fine filaments.

In the second class of applications however the penetration depth may be small, one is now at the right of the peak and the best way to reduce losses may be to increase ϵ i.e. large filaments. For example, in a magnetically levitated vehicle, the ΔB caused by guideway irregularities is expected to be of the order of 0.02T. If we assume a DC field of 5T i.e. $J_c = 1.5 \times 10^9$ A m^{-2} and a filament diameter of 50μ i.e. $a = 25 \times 10^{-6}$m, we find $\epsilon = 2.36$, a dimensionless loss of 0.57 and an actual loss Q of 90 J m^{-3} (0.09 mJ/cm^3) per cycle. At a frequency of 50 Hz this would disipate 4500W m^{-3} (4.5 mW/cm^3) which is very similar to the loss in a synchrotron magnet. This loss may be halved by simply making the filament twice as big i.e. 100μ dia. In order to halve the loss by reducing diameter however it would be necessary to make $\epsilon = 0.075$ i.e. a filament diameter of only 1.6μ or roughly 4000 times as many filaments as the 100μ case! Clearly the most economical way to reduce losses in this case will be to make the filaments as large as possible. Even at 50μ diameter however there is some danger of instability and at 100μ diameter there will probably be flux jumping. Stability thus provides the upper limit to filament size and the exact value of this will depend on other parameters such as operating field, proportion of copper in the conductor etc.

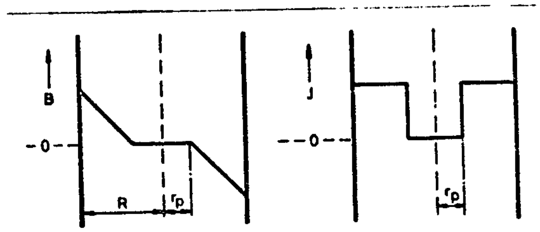
It is dangerous to generalize about filament size however. In the fusion reactor application for example, one might have a DC background field of 7.5T and a pulsed field of 0.5T(3). In this case we have $J_c = 5 \times 10^8$ A m^{-2} and hence $p = 800\mu$; even with a 100μ diameter we find $\epsilon = 0.0625$ and are thus far to the left of the peak in Figure 1. Any reduction in filament size will therefore reduce the losses; any feasible increase in filament size will increase losses.

Similar considerations also apply to the coupling of filaments through the matrix of the conductor. Roughly speaking, when the filaments are well coupled, they behave co-operatively as one single large filament. Thus, in certain cases the loss may be reduced by increasing the coupling between filaments. For example Satow, Tanaka and Ogama(4) have found that under some conditions the losses in untwisted composites can be less than in twisted composites. Stability could be a problem in this case of course. Again it is impossible to generalize and each condition must be treated individually.

3. STABILITY

Magnetic instabilities or flux jumps can drastically degrade the performance of a magnet although of course they are not the only cause of degradation; mechanical movement is quite certainly another. In recent years the mechanisms of cryostatic stabilization and of intrinsic adiabatic stability have become rather well understood. The coupling of filaments in a composite in response to an external field and its effect on stability are also understood. The self field coupling and consequent self field instability is still however less well understood. Self field effects are important because they limit the overall size of a composite. Significant advances in the theory of self field effects have recently been made however by Turck and Duchateau and their work will be referred to frequently in this section.

Very briefly, the self field effect is the tendency for the transport current in a filamentary composite to flow preferentially in the outer regions of the composite and to only penetrate inwards when critical current density is reached at the outside. The current and field distributions in the composite are therefore as shown in Figure 3. This 'piling up' of critical current in the outermost filaments tends to be unstable. It is not possible to encourage a more uniform sharing of current by simply twisting the composite. To achieve this, a full transposition of the filaments is needed whereby the inner filaments pass to the outside and vice versa as one moves along the composite.



(a) field distribution. (b) current distribution.

FIG. 3. Self field patterns in twisted composites

On applying a simple adiabatic stability theory to the situation illustrated in Figure 3, one is forced to conclude that a typical filamentary niobium titanium composite will be unstable at composite diameters greater than ~ 0.5 mm. Practical magnet experience shows that this is clearly not the case. Two main reasons may be advanced for the failure of the simple theory; firstly the self field flux jump is not adiabatic and secondly, the current distribution is not as simple as the one shown in Figure 3. The newer theories take account of both these effects. In order to illustrate their scope and limitations, they will now be applied to two different conductors which have been tested in several medium sized solenoids at the Rutherford Laboratory.

<u>3.1 Experimental Tests.</u> The first conductor tested was a 1000 filament (IMI B1000), 1 : 1 matrix: superconductor ratio, 2 mm diameter composite, twisted at a pitch of 25mm. Three solenoids were fabricated from this conductor, each of 100 mm bore, resin impregnated and producing a peak field of about 6T. All the magnets showed some training - between one and four quenches - but quickly reached their short sample current. The subsequent quench currents were surprisingly constant to better than 1 in 10^3: a good indication that no instabilities were present. At each quench, the whole magnet was heated above critical temperature so that the current distribution in the superconductor started each time from the virgin state. This means that the training which was seen could not have been primarily electromagnetic but was probably mechanical.

The theory of Turck and Duchateau treats a cylindrical composite carrying a current distribution like that shown in Figure 3. Full account is taken of the magnetic damping in the matrix which slows down the progress of the flux jump and of the thermal conduction processes which remove the heat generated by flux motion in the superconductor. The thermal conditions at the boundary may either correspond to the composite being cooled by liquid or gaseous helium or immersed in a resin impregnated winding. The major factor determining stability is the parameter β defined in (5) or (6) as

$$\beta = \frac{\mu_o (\lambda J_c)^2 R^2}{c\, \theta_c}$$

where λ is the space factor of filaments in the composite, R is the outer radius of the composite, c is the specific heat and θ_c is the critical temperature rise defined by

$$\theta = -J_c \cdot \frac{d\theta}{dJ_c}$$

(note that some of Turck's symbols have been changed to avoid conflict with the rest of this paper) For the composite in question, at a field of 6T we find $\beta = 48$. Referring now to Figure 12 in ref. (6), we may infer that the composite should become unstable in a resin impregnated magnet when the current flowing in the outer region reaches 70% of the critical current of the composite, i.e. when the inner boundary of this region r_p has moved in to a radius of 0.55 mm.

This is not the whole story however because a more detailed consideration of the current distribution within the composite will show that one might also expect additional currents to flow in the region $r < r_p$. This is brought about by the way in which the self field and external field can interact with the magnetization and transport currents within the individual filaments to cause a shift in the 'electric centre line' of the filament, (7)(8). In this way, a current distribution will be induced to flow in the central region. Because these currents are subcritical, they will be quite stable and the composite will thus be able to carry this additional transport current with unimpaired stability.

In order to determine the magnitude of the internal currents we refer to Figure 9 of ref. (7). This shows how the internal subcritical currents in the composite increase with radius until at a certain radius they reach critical. The boundary conditions between the two regions will then be perfectly matched if this radius, a, is set equal to the penetration radius r_p of the outer region. Thus we may substitute $a = r_p$ into equation (9) of ref. (7).

$$\beta_w = \left\{\frac{2\mu_o \lambda J_c}{B_e d}\right\}^{\frac{1}{2}} a$$

where the original β has been written as β_w to distinguish it from Turck's β, B_e is the external field, d the filament diameter. For the composite in question with $\lambda = 0.5$, $J_c = 1.03 \times 10^9$ A m^{-2}, $B_e = 6$T, d = 45μ and $a = r_p = 0.55$ mm we find $\beta_w = 1.20$. This value of β_w may now be used to find the total current induced in the region $r < a$. Figure 10 of ref. (7) shows f as a function β_w where f is the total induced current expressed as fraction of the critical current of the inner region. For $\beta_w = 1.20$ we find f = 0.84.

The final result of all this is that we would expect the 2 mm composite to stably carry up to 70% of its critical current in an outer sheath flowing at critical density. The inner region of the composite would carry stable sub-critical currents up to 84% of the critical current of the inner region or 0.84 x 30% = 25% of the entire composite. The maximum stable current for the composite would thus be 70% + 25% = 95% of critical. The fact that the magnets actually reach critical current is therefore perhaps not too surprising.

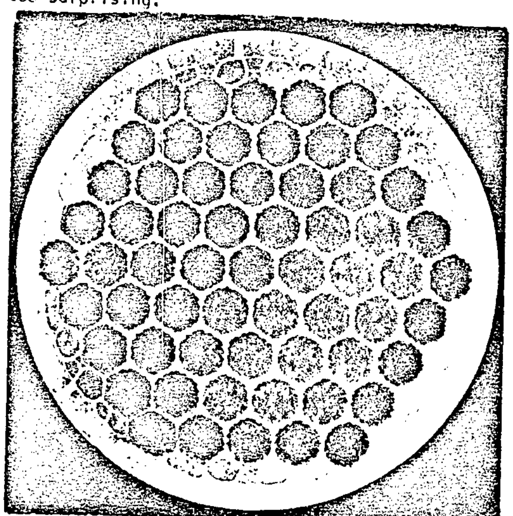


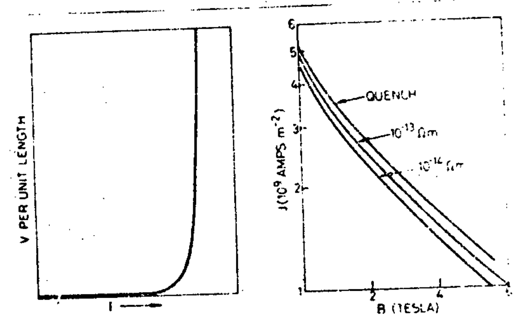
FIG. 4. The 3.5mm dia. 14701 filament composite used in self field rest solenoid.

The second magnet result is surprising however. This was a solenoid of similar size which was made to test the large three component composite shown in Figure 4. The composite was 3.5 mm diameter containing 14701 filaments with 39% of NbTi, 39% of copper and 22% of cupro-nickel. After some training the magnet reached [illegible]% of its 'short sample' field, the current carried was 87% of critical.

Applying the theory of Turck and Duchateau to this magnet we find $\beta = 133$, predicting an instability in the outer sheath when it carries a current of $\sim$ 50% of the critical of the whole composite, i.e. $r_p = R/\sqrt{2} = 1.24$ mm. Because the filaments are much finer in this composite, the 'electric centre' effect is less than before. We find $\beta_w = 7.2$ and hence f = 0.26. This inner region will thus only carry 26% of its critical current in a stable sub-critical fashion before it reaches critical density at its outer boundary. We therefore expect the composite to become unstable at 50 + 0.26 x 50 = 63% of its critical current. In this case it is clear that, in spite of its many corrections and greater thoroughness, the theory is still too pessimistic.

3.2 Decay of the Self Field Current Distribution.

A possible explantation for this which does not seem to have been mentioned so far is that the ideal current distributions assumed in (5) and (6) might decay rather rapidly in a magnet. This could be brought about by the 'resistive transition' effect illustrated in Figure 5. Although it is not well understood, this effect is thought to be shown by all multifilamentary superconductors. As critical current is approached the composite does not switch sharply to the resistive state but rather undergoes a gradual transition in which a measureable resistance in progressively developed from ~ 80% of critical current density upwards. It seems reasonable to suppose therefore that any array of filaments, carrying critical current density will develop a resistance. The outer sheath of critical current would thus be resistive.



(a) voltage - current curve (b) lines of constant resistivity

FIG. 5. Resistive transitions in filamentary NbTi composites

The usual mechanism postulated for the decay of the self field current distribution is that the current, as it is fed into the composite at the magnet terminals, must cross the matrix. The transverse resistance of the matrix will thus cause the purely inductive current distribution which is initially set up to decay with a time constant

$$\tau = \frac{\mu_o}{\rho_m} \cdot \frac{\ell^2}{4}$$

where ρ_m is the mean transverse resistivity of the matrix and ℓ is the length of the composite. The composite shown in Figure 4 had an unusually high transverse resistivity of $\sim 10^{-8}$ Ωm and the coil was wound from a very short length of conductor - only 36 M. Even in this case however the decay constant is $\sim 4 \times 10^4$ secs. The magnet was actually taken to its quench current in 26 secs. It is clear that the matrix resistivity, even though it was exceptionally high, could not have caused any significant decay of the self field current distribution. Most magnets, with lower matrix resistivities and longer lengths of conductor will have much longer time constants.

Much shorter time constants are found however if it is assumed that the filaments in the outer sheath are developing an effective longitudinal resistivity. For the 3.5 mm diameter composite carrying 50% of I_c in a critical outer sheath we may roughly calculate that the time constant for this to decay into the inner region is

$$\tau \approx \frac{\mu_o R^2}{4\rho_e} \cdot \ell n\left[r_1/r_2\right]$$

where r_1 and r_2 are the mean radii of the outer and inner regions and ρ_e is the effective longitudinal resistivity of the array of filaments. Note that this time constant does not depend on the length of conductor. As shown in Figure 5(b), a typical composite might develop a resistivity of 10^{-13}Ω m at 95% of its ultimate quench current and 10^{-14}Ω m at 90% of I_c. For $\rho_e = 10^{-13}$Ω m we thus find $\tau \approx 5$ secs.

It is clear therefore that within a rather short space of time, the potentially unstable outer current sheath will have decayed to a more stable sub-critical level - perhaps to 95% of the critical current density. This process will continue with a gradually increasing time constant until the distribution of current is uniform over the cross section. One would therefore expect it to be stable, at least against small disturbances.

Note that this in no way contradicts the theory of Turck and Duchateau. Nor is it in disagreement with the results of their experiments which were performed on fairly short samples of conductor. The experiments did in fact indicate that the non-uniform current distribution decayed with time. It was assumed however that this would not happen in magnets involving long lengths of conductor.

An interesting possibility arises from the idea of a partial decay of the self field current distribution. Let us assume that the magnet containing the 3.5 mm composite is being charged and has reached, say, 70% of its critical current. The composite would be unstable and would quench if its outer current sheath were flowing at critical density as assumed in the theory. This outer sheath has however decayed resistively to 95% of critical density and it is stable. Suppose now that a local energy release in the magnet

suddenly raises the temperature of the composite by just the amount needed to reduce the critical current density of the superconductor by 5%. The outer sheath will now be at critical current density, it will be unstable and will quench. Our small (5%) temperature rise has thus been able to quench a conductor which is only at 70% of critical. In other words, large diameter filamentary composites, although they may not actually be self field unstable, will be more than usually vulnerable to small temperature fluctuations within the magnet, e.g. mechanical movement effects.

It is possible that such an effect has already been seen by the workers at Fermi Laboratory where magnets wound from a large twisted composite have been seen to train much more than similar magnets made from transposed cable(9).

4. NIOBIUM TIN

Niobium tin tape has been available commercially for several years and has been used in the construction of all the large high field superconducting magnets currently in use. It does however have the disadvantage that it is basically unstable in the presence of magnetic fields perpendicular to the broad face of the tape. This instability may be controlled by soldering copper strip to the face of the tape (dynamic stability) and arranging for the edge of the strip to be cooled by liquid helium. The charge times of such magnets can be long however ($\sim$ 1 hour) and the need for edge cooling can cause difficulties in some types of coil geometry.

Filamentary niobium tin can be expected to be much more stable than the tape and is now being actively pursued in many places. An unusual 'filamentized' niobium tin tape has recently been made by IGC(10) and is shown in Figure 6. The subdivision of the tape has been achieved by a chemical milling process. It is interesting to note that, whereas conventional tapes showed a strong tendency to flux jump in normal fields, no flux jumps were observed in the filamentized tape. It is not clear however whether tapes of this kind can be produced economically in long lengths and to a consistent standard of quality.

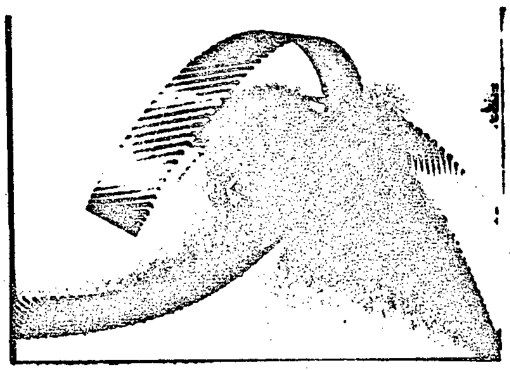


FIG. 6. 'Filmentized' Nb_3Sn tape

A more popular approach to the production of filamentary Nb_3Sn has been the use of the 'bronze route'. In this process, filaments of pure niobium are drawn down in a tin copper bronze. At its final size, the wire is heat treated for typically $\sim$ 100 hours at 550°C - 750°C so that the tin in the bronze reacts with the niobium filaments to form filamentary niobium tin. Not only does this process offer a very convenient way of producing the brittle Nb_3Sn in filamentary form but it can also ensure that the Nb_3Sn so produced is of good quality. At reaction temperatures below 930°C the only compound of niobium and tin to form in the bronze process is Nb_3Sn (cf. the liquid tin process where Nb_6Sn_5 and $NbSn_2$ normally form below 930°C). Because the bronze process is a solid state reaction, the resulting filaments of Nb_3Sn can be very smooth and uniform. Because the reaction takes place at low temperature, the grain size of the Nb_3Sn so produced can be small and its critical current density large.

An interesting variation on the bronze method has recently been demonstrated by Tsuei(11). In this process, a filamentary structure is produced metallurgically by first chill-casting an alloy of Cu,Sn and Nb and then working it down to finished size, when a final heat treatment is applied to form Nb_3Sn. Unfortunately the overall current densities exhibited so far by these composites are very low. If they could be improved, the method would clearly be a very cheap way of producing multifilamentary Nb_3Sn.

4.1 Current Density. Figure 7 shows a typical overall current density for a bronze matrix niobium tin composite. Considerable effort is currently being put into the optimization of this process and there is probably scope for the improvement of J_c. It is generally felt that the basic problem is one of obtaining good stoichiometry throughout the layer while at the same time keeping a fine grain size. Flux pinning is thought to occur at the grain boundaries so that a small grain size should mean a high density of pinning points.

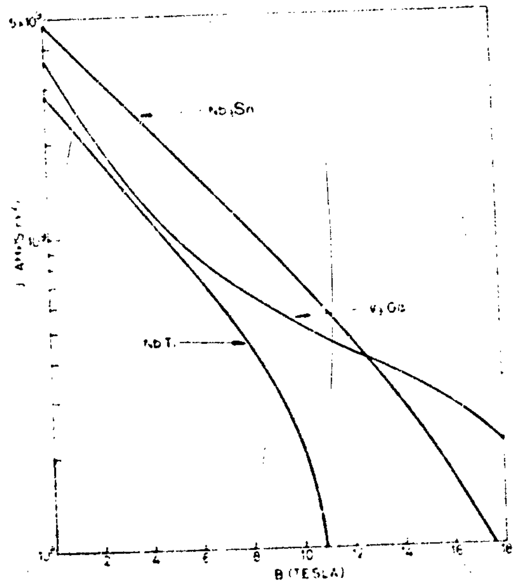


FIG. 7. Overall current densities of filamentary composites

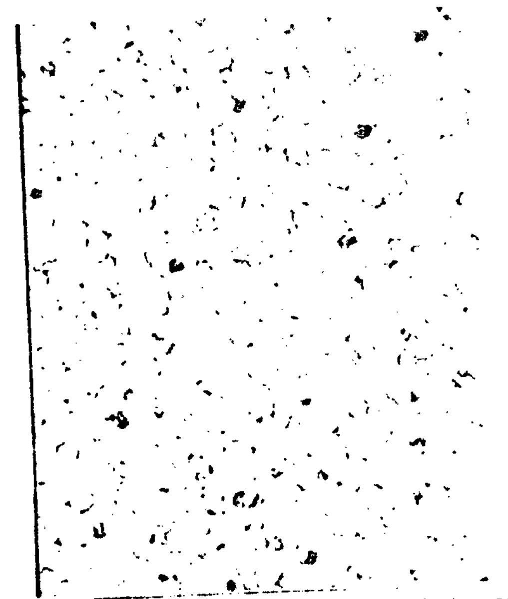


FIG. 8. Reacted filaments of Nb_3Sn in bronze

If the heat treatment is terminated before complete reaction, the resulting filament will have a pure niobium core as shown in Figure 8. This is thought to confer good mechanical properties on the composite but is thought to not produce the best superconducting properties because there will be a variation in stoichiometry across the Nb_3Sn with a niobium rich layer adjacent to the unreacted core. A hint that this is indeed the case can sometimes be seen by measuring the critical temperature of the composite by both inductive and resistive methods. It is often found(12) that, whereas the resistive measurement shows a sharp transiti n at ~ 18 K, the inductive measurement indicates a gradual transition spread over several degrees up to 18 K. One might thus infer that the filament contains several layers of different T_c but that most of the current is carried in the stoichiometric high T_c layer. The longer times or higher temperatures needed to produce a more stoichiometric compound might however also produce grain growth with a consequent reduction in J_c.

On the basis of the above arguments, it would appear that the best way to obtain a high current is to use very fine filaments of niobium which can be reacted to completion at lower temperatures and in shorter times. This has yet to be conclusively demonstrated in practice. Another approach is to dope the niobium with small quantities of zirconium or zirconium oxide whichis expected to retard the rate of grain growth in the Nb_3Sn. It has been found(13) that, although the Zr additions are effective in raising the current density of thick layers of Nb_3Sn, the highest current densities are still found in the thinnest layers of undoped material.

When seen from the point of view of the magnet technologist of course the important current density is not the J_c of the Nb_3Sn compound but the overall J_c of the composite. It is not practical to draw down a brc ize which contains more than ~8 at % of tin because of the brittle intermetallics which form above this level. It has been found that the Nb_3Sn reaction will continue until about 0.3 at.% of tin remains in the bronze. From these two figures we may calculate that the maximum filling factor of the reacted Nb_3Sn filaments in the composite can only be about 33%. In practice it has so far been nearer 10%-20%. It is interesting to speculate on what the highest possible overall current densities might be. If we take the highest J_c in the Nb_3Sn observed in filamentary composites(13) as ~ 5.5 × 10[illegible] A m^{-2} at 10T and multiply this by the filling factor of 33% we obtain an overall J_c of 1.8 × 10[illegible] A m^{-2}, a factor of ~ 2½ better than the 7.5×10^8 A m^{-2} plotted in Figure 7. It is however by no means clear whether this performance can be achieved in a practical conductor. All the above figures neglect the diluting effect of the additional regions of pure copper which will be needed in any large magnet conductor.

The surface diffusion process offers a way of increasing the final proportion of Nb_3Sn in the composite

by allowing a higher tin content in the bronze so that more niobium may be reacted to completion. After processing to final size the composite is given a surface coating of tin and is heated to an intermediate temperature to allow the tin to diffuse into the composite. It doesn't matter if the bronze becomes brittle at this stage because all the drawing processes have been finished and higher tin concentrations are ... ssible. Indeed it is not even necessary to draw down bronze at all; a pure copper matrix may be used and all the tin finally added by coating. This has manufacturing advantages because pure copper is much easier to work than bronze. Using this process, McInturff and Larbalestier(14) have achieved the highest ... all current densities so far reported for filamentary Nb_3Sn : 3×10^9 A m^{-2} at 5T.

Another approach, recently described by Hashimoto, Yoshizaki and Tanaka(15) makes use of a very tin ... bronze to provide a 'reservoir' of tin. A single rod of Sn-20 at % Cu is placed inside a copper tube ... has many thinner rods of pure niobium embedded in its wall. The whole composite is drawn down to finished size and then heated to ~ 750°C. During this heat treatment the tin diffuses into the copper and then reacts with the niobium. One advantage of this process is that all the starting materials are much more ductile than Cu-8 at.% Sn bronze and the drawing down to final size can be performed without the need ... frequent heat treatments. Another advantage could be that, like surface diffusion, this process could ... a greater proportion of Nb_3Sn in the finished composite.

<u>... Stabilization and Protection.</u> It is an unfortunate fact of life that the Nb_3Sn reaction appears to ... off when the proportion of tin in the bronze falls to ~ 0.3%, giving a residual resistivity of ... If it were possible to 'clean out' the bronze and leave only pure copper with a resistivity ... 10^{-9} - 10^{-10} Ω m, the matrix would be able to perform the two very useful functions of stabilizing ... composite and protecting it from burn out at quench in a magnet. Instead, it has so far been necessary ... add pure copper to the matrix as a separate item. Because the tin in the bronze is very mobile at the reaction temperature, it is essential that the pure copper is protected from the bronze by a diffusion barrier of tantalum or some other metal. One may choose to have islands of copper surrounded by a barrier ... a matrix of bronze, like the Harwell composite(16) shown in Figure 9. Alternatively the bronze and superconductor may be divided into islands, surrounded by a diffusion barrier and immersed in a copper matrix, like the Airco composite(17) shown in Figure 10. The former arrangement normally gives the lowest ... losses whereas the latter allows a higher proportion of copper in the matrix. A third approach, used ... the IMI composite(18) shown in Figure 11 and also being pursued by Supercon and Westinghouse(19) is to use the niobium itself as the barrier. Each filament is now a hollow tube of niobium containing bronze and immersed in a matrix of copper. Reaction takes place on the inner surface of the tube and, provided it does not go too far, the copper outside should remain uncontaminated.

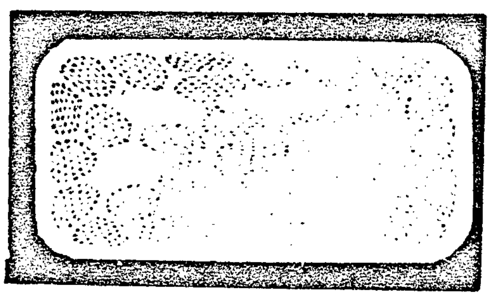


FIG. 9. Harwell multifilamentary Nb_3Sn with islands of pure copper in bronze matrix

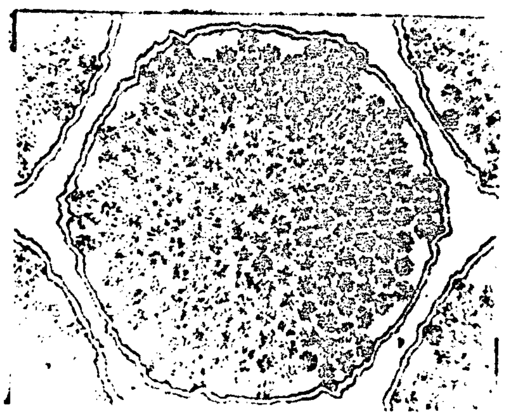


FIG. 10. Region of an Airco multifilamentary Nb_3Sn with clusters of filaments in bronze, grouped in copper matrix.

If the composite is to be made into a stranded cable, the copper can be added as separate strands in the cable, as for example in the cable made by IGC(20). To avoid mechanical damage to the Nb_3Sn it is preferable to make the cable before reaction, so that the copper strands must again be protected by a barrier. Finally, it is possible to simply plate copper onto the reacted composite. Both the plating and the cabling techniques will certainly help to protect the composite from burn out at quench but the copper may be too far away from the filaments to provide much dynamic stability. The plating technique also precludes any possibility of reacting the composite after winding the magnet.

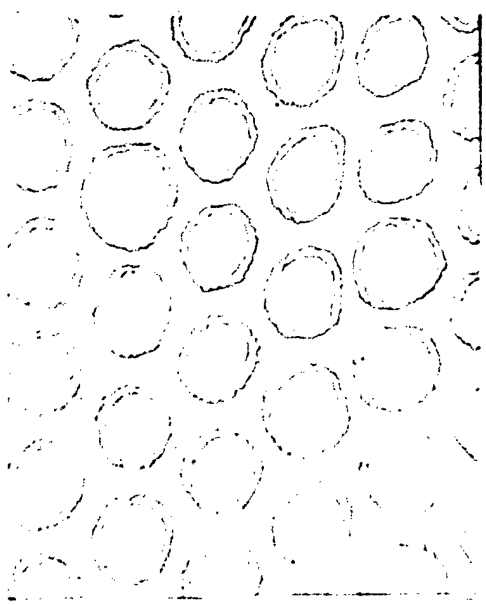


FIG. 11. Region of an IMI multifilamentary composite, niobium tubes containing bronze in a pure copper matrix (unreacted)

4.3 Dynamic Stability. Copper in the matrix will help stability by providing magnetic damping to slow down a flux jump and thus allow more time for the heat generated to diffuse away. For this to happen, the copper must be sufficiently close to the superconductor to slow down the motion of flux within it. We may make a very rough estimate of how close this should be by applying the dynamic stability criterion(21)

$$d < \left\{\frac{8\theta_c k(1-\lambda)}{\rho\lambda\, J_c^2}\right\}^{\frac{1}{2}}$$

where d is the stable filament diameter, k is the thermal conductivity of the superconductor, ρ is the copper resistivity. For composites like the one shown in Figure 10 we are concerned with clusters of filaments rather than individual filaments. In this case, provided the filaments are relatively fine, it is probably a fairly good approximation to consider the whole cluster as a single 'macro filament'. The values of J and k should then be taken as a suitable weighted mean between bronze and Nb_3Sn. The filling factor λ is now the fraction of the whole composite occupied by the Nb_3Sn and bronze together. Using figures for a typical composite at 5T, we find $d \sim 400\mu$. This is the maximum cluster size at which the copper will be effective in damping down instabilities, e.g. self field flux jumps. For the other geometries we may perhaps adopt a general rule of thumb that no Nb_3Sn filament in bronze should find itself more than 200μ away from a region of pure copper.

4.4 Mechanical Properties. Niobium tin is a brittle material; this poses severe problems in coil winding and also in supporting magnetic field stresses in the finished magnet. In bulk form, Nb_3Sn breaks at a tensile strain of about 0.2%. It is certainly better than this in filamentary form but opinion is still somewhat divided as to how much better it is. Several workers(12,19,20) report that strains of up to 1% can be imposed before there is any noticeable reduction in current carrying capacity. Others have seen damage at strains as low as 0.3%(22). At the Rutherford Laboratory we have found that the amount of degradation seen can depend very strongly upon the sensitivity of the measurement(23). Although a strain of 0.67% caused only a small reduction in the quench current of a short sample, it reduced the current at the 10^{-14} Ω m detection level by almost a half. In a fully impregnated magnet, the composite would be expected to quench at somewhere between the 10^{-13} Ω m and 10^{-14} Ω m short sample currents. The exact level will depend on the local thermal environment at the high field point in the magnet. It is therefore important, when assessing the amount of damage caused by straining a wire, to carry out a proper resistive transition measurement. The quench current of a well cooled short sample can be a very poor guide to the quench current of an impregnated magnet.

It is almost certain that filaments which are only partly reacted will exhibit better mechanical properties than fully reacted filaments. In this case, the unreacted niobium core probably serves to halt the propagation of cracks originating at the surface of the filament. It also seems likely that the filaments are generally under a compressive strain of ~ 0.2% caused by their differential contraction with respect to the matrix on cooling down from the reaction temperature. This can only help the mechanical properties of the composite.

Opinion is also divided on the question of whether it is better to react the wire first and then wind the magnet or wind first and then heat the whole magnet. At Rutherford, we are especially interested in the construction of dipoles and quadrupoles for beam transport. In these magnets, the minimum bending radius at the coil ends can be as small as 5 mm so that, even at 1% strain, a reacted conductor could only be 0.1mm in diameter. We have therefore chosen to react the whole magnet after winding and feel that the need to use heat resisting insulation and coil formers is a small price to pay for the avoidance of risks associated with winding reacted conductor. We use E glass fibre insulation, either braided or lapped. In order to protect the glass from abrasion during winding, it is desirable to use some kind of binder to glue the fibres together. We are presently trying to find the best binder; one which can be easily applied to the conductor and which will volatilize cleanly at the heat treatment stage without leaving

leaving a conducting residue of carbon, or oxidizing the conductor. The most promising candidate at present seems to be perspex.

Many other groups have opted for the alternative 'react first and wind later' technique. In this case the diameter of the wires must be small to avoid filament damage on bending. If such fine wires are wound singly into a magnet of reasonable size, there will be protection problems. For example, if the 0.1 mm wire already mentioned were used to make a dipole magnet of stored energy $\sim$ 1 M Joule, the peak internal resistive voltage at quench might be $\sim$ 1 MV, even if the composite contains $\sim$ 20% of pure copper. It is clearly necessary to increase the operating current and reduce the coil inductance by using many strands in parallel as a braid or cable. The cable may be impregnated with indium or similar metal after reaction. It would appear that the resulting cable can be almost as flexible as its component strands, i.e. that the minimum winding radius is determined by the diameter of the individual wires rather than the diameter of the cable(20)(24).

If the conductor is intended for the fabrication of a large magnet with large bending radii, such as a bubble chamber, there seems to be little doubt that it can be reacted before winding. Care will still be needed however to avoid any local kinking of the conductor.

5. VANADIUM GALLIUM

The critical current density of vanadium gallium falls off with field much less rapidly than that of niobium tin. When viewed in terms of overall current density as shown in Figure 7, the two curves cross over at around 12.5 T, giving V_3Ga the advantage at high fields. At 17 T for example, a V_3Ga composite has twice the overall current density of Nb_3Sn. The flatter shape of the J_c curve is also generally to be preferred on grounds of stability and hysteresis loss. Against these advantages however must be set the lower T_c of V_3Ga : 14.5 K as against 18 K for niobium tin and the significantly higher cost of vanadium and gallium in comparison with niobium and tin.

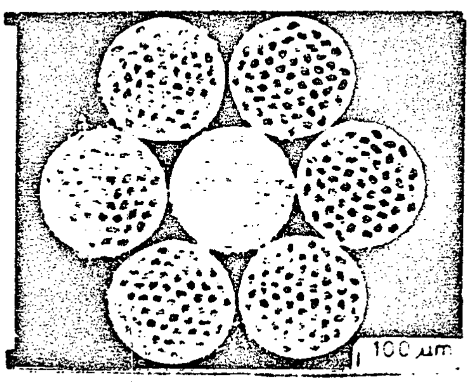


FIG. 12. Furukawa multifilamentary V_3Ga cable, six composite twisted around a tungsten wire.

V_3Ga tapes were probably the first superconductors to be made using a bronze process. It was found(25) that the rate of growth of the V_3Ga layer and also its critical current could be markedly increased by copper plating the gallium coated vanadium wire before heat treatment. The bronze technique was subsequently applied to the first commercial production of multifilamentary A15 compound superconductors: the V_3Ga composites and cables made by the Furukawa Electric Company(26). Figure 12 shows a cross section of one of these cables. The centre strand is a tungsten wire, for strength; the six outer strands are composites of 55 filaments of vanadium in gallium bronze. After reaction the cables are impregnated with indium. Overall densities are as plotted in Figure 7.

5.1 Current Densities. Although the overall current density of V_3Ga composites at medium fields is presently rather disappointing, this situation could be quite dramatically changed by the recent work of Howe and Weinman(27). These workers have evolved a technique in which both the vanadium core and the copper matrix are alloyed with gallium, e.g. 9 at.% Ga in the vanadium and 17.5 at.% Ga in the bronze matrix. In this way, the reaction temperature may be reduced from $\sim$ 600°C to $\sim$ 550°C. As a consequence of the lower temperature of formation, the critical temperature has been found to increase by $\sim \frac{1}{2}$ K and the critical current density by a factor of $\sim$ 5. The maximum current density observed at 10 T was in fact 10^{10} A m^{-2}.

In spite of their high local current densities, the filling factors of these experimental composites is low (as shown in Figure 13) and their overall J_c would not be very interesting to the magnet constructor. At present, one can only speculate on what the maximum overall current density in a practical magnet conductor using this process might be. If, for example, one could start with 20 at.% of gallium in the bronze and then react until this level had fallen to 10 at.% and all the vanadium was consumed, the resulting filaments of V_3Ga would occupy $\sim$ 25% of the composite cross section. If the highest current densities could be obtained over the whole cross section of each filament, the current density at 10 T over the composite would be 2.5 x 10^9 A m^{-2}. A spectacular figure, but there are many 'ifs' in the argument leading up to it.

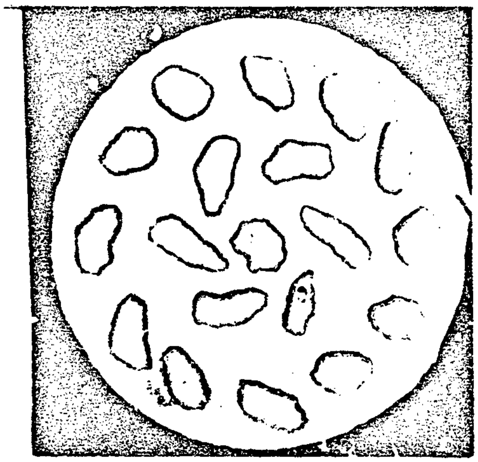


FIG. 13. Experimental high J_c composite of V_3Ga

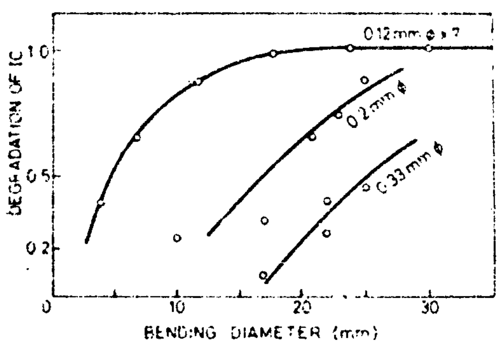


FIG. 14. Bending properties of V_3Ga composites

It has also been found by Tachikawa Itoh and Tanaka(28) that the addition of 1-5 at.% of aluminium to the vanadium filament can markedly increase the rate of formation of V_3Ga and raise its critical current density.

5.2 Stabilization and Protection. The V_3Ga reaction is thought to stop when the gallium content of the bronze falls to about 10 at.%. At this concentration, the resistivity of the bronze is reported to be ~ 10^{-7} Ω m at 4.2 K. This is almost as high as the cupro-nickel used to provide resistive barriers in AC NbTi composites. It is not surprising therefore that the pulsed behaviour of multifilamentary V_3Ga is good.

If the composite is to be used in the construction of a magnet of reasonable size however, some pure copper or other good normal conductor will be needed for protection from burn-out at quench. Any composite or cable of diameter greater than, say, ½ mm would also benefit from the stabilizing influence of a high conductivity component. The indium coating on the Furukawa cable is thought to confer a degree of stability but for large magnets and cables, something of lower resistivity will be needed. To the author's knowledge, no such cable or composite has yet been produced.

5.3 Mechanical Properties. The mechanical properties of V_3Ga appear to be very similar to those of Nb_3Sn. Figure 14 shows the degradation of critical current in two different wires and a cable as they are bent around various diameters (29). From this data, it would appear that the filaments can be strained to ~ 0.7% without damage and also that the minimum permissible bending radius of a seven strand cable does not differ appreciably from that of its component strands. One should again beware however of the difference in quench current between a well cooled short sample and a fully impregnated magnet.

6. DISCUSSION AND FUTURE PROSPECTS

It seems likely that multi-filamentary composites will continue to be the most common type of superconductor used in magnet construction. New requirements for low losses in small amplitude AC fields may however demand different designs for such applications as magnetic levitation. The theory of magnetic instabilities in filamentary composites has been improved and extended in recent years and is now fairly well understood. The major cause of degradation in magnets however is now mechanical - small movements, ..., cracking etc. causing a local release of energy. This is not very well understood at present ... more work is needed in this area. Magnetic stability theory should at least be able to tell us which conductors might be especially vulnerable to these mechanical effects.

Filamentary Nb_3Sn and V_3Ga are advancing to the stage where they must be considered as useful magnet conductors. Many of the problems of production and utilization have been sorted out and we may confidently expect to see these materials used in the construction of several medium sized magnets before the next Magnet Technology Conference. These is undoubtedly scope for a further improvement in the current carrying capacity of these materials; it will be disappointing if a further factor of two in overall J_c is not forthcoming in the fairly near future.

In the longer term, perhaps the most exciting prospect is the promise shown in Figure 15 - Nb_3Ge: critical temperature 23 K, upper critical field 38 T. Even at a temperature of 18 K, the critical current density is quite respectable and at lower temperatures it is probably very high indeed.

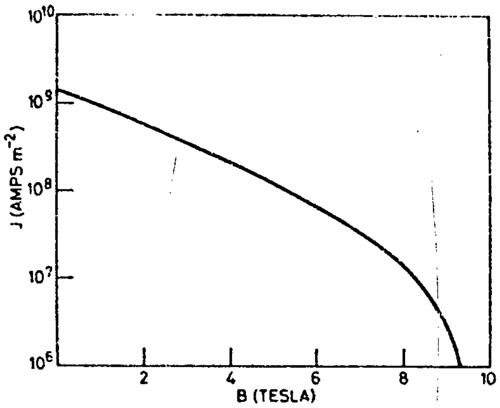


FIG 15. Nb_3Ge current density at 18 K

It is very difficult to form stoichiometric Nb_3Ge and the low critical temperatures measured in the past can be attributed to non-stoichiometric compound. Recently however, Gavaler(30, 31) has shown that it is possible to make stoichiometric Nb_3Ge using a sputtering process under very carefully controlled conditions of gas pressure, voltage and temperature. It would be difficult to maintain such strict control in any kind of continuous process. Present indications are that Nb_3Ge cannot be made by a bronze process but this is by no means fully established, possibly a matrix other than copper may yield a satisfactory result. However, in view of the very recent nature of these discoveries, it is really not very useful to speculate on production techniques at this point in time. One can probably say with some confidence however that in the next few years, while the magnet technologists are grappling with the problems of using the present 'exotic' materials Nb_3Sn and V_3Ga, the more basic research work is going to find several new materials offering greatly improved H_c, T_c and J_c and that at least one of these will prove to be technologically useful.

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